

OPIC  
OFFICE DE LA PROPRIÉTÉ  
INTELLECTUELLE DU CANADA



CIPO  
CANADIAN INTELLECTUAL  
PROPERTY OFFICE

Ottawa Hull K1A 0C9

(21)	(A1)	2,142,195
(22)		1995/02/08
(43)		1996/08/09

(51) Int.Cl. <sup>6</sup> D21H 25/18

(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Deacidification of Cellulosic Material

(72) Worsfold, D. James - Canada ;

(71) Same as inventor

(57) 20 Claims

**BEST AVAILABLE COPY**

**Notice:** This application is as filed and may therefore contain an incomplete specification.



Industrie Canada Industry Canada

Canada

2142195

DEACIDIFICATION OF CELLULOSIC MATERIAL

ABSTRACT

A composition for deacidification of aging cellulosic materials, such as paper, books, documents, works of art, clothing and flags, from library, archive and museum collections is comprised of a carbonated magnesium alkoxide, such as methoxymagnesium methylcarbonate or ethoxymagnesium ethylcarbonate, a solvent, such as methanol or ethanol, and a hydrochlorofluorocarbon and/or a hydrofluorocarbon diluent. The deacidification composition of the present invention may be applied by spraying through a nozzle, by brushing or by immersing the cellulosic material in the deacidification composition.

## DEACIDIFICATION OF CELLULOSIC MATERIAL

## FIELD OF THE INVENTION

5 The present invention relates to the field of preservation of cellulosic materials, such as books, documents, works of art, clothing and flags, and in particular, to a process for deacidification of cellulosic materials.

## 10 BACKGROUND OF THE INVENTION

There is much concern about the deterioration of aging cellulosic materials, particularly those of library, museum and archive collections. The most significant cause of deterioration of cellulosic materials is acid-catalyzed hydrolysis of cellulose which results in shortened cellulose molecules, and weak and brittle fibres. There are a number of factors which cause an acidic condition in cellulosic materials including air pollutants, the use of alum in the paper-making process and the degradation products of cellulose and ink.

20 In an effort to reduce the deterioration of cellulosic materials by acid-catalyzed hydrolysis, researchers have turned their attention to processes for deacidification of cellulosic materials. Attention has been specifically directed to non-aqueous deacidification compositions to neutralize the acidity of the cellulosic materials and to introduce an alkaline reserve to inhibit re-acidification.

United States Patent Number 3,676,182 (R.D. Smith, July 11, 1972) relates to a process for non-aqueous deacidification of paper using magnesium methoxide as a deacidification agent. The deacidification agent is dissolved in methanol to a concentration of about 5 to 11%. The resultant solution may be diluted with a chlorofluorocarbon, such as trichlorofluoromethane or dichlorodifluoromethane, to produce a solution of about 1 to 2% magnesium methoxide. The chlorofluorocarbon contributes to rapid evaporation of the solution and

imparts hydrophobic properties to deacidification solutions containing methanol, thereby minimizing attack on certain inks by methanol. Books and papers may be dipped in the solution or the solution may be applied by brushing or spraying.

However, magnesium methoxide is extremely sensitive to water such that even traces of moisture cause immediate hydrolysis and a gelatinous precipitate of magnesium hydroxide which is insoluble in water and inorganic solvents. Unless the paper is sufficiently dried prior to treatment, premature hydrolysis of the magnesium methoxide may occur, causing an undesirable glaze of magnesium hydroxide to be formed on the surface of the paper. Furthermore, the nozzles of spray guns are subject to frequent plugging. The bristles of brushes also become clogged and must be cleaned and dried prior to reuse.

United States Patent Number 3,939,091 (Kelly, G.B., February 17, 1976) discloses a composition for use in the deacidification of paper which overcomes the problem of the prior art deacidification solutions comprised of magnesium methoxide dissolved in a chlorofluorocarbon. Magnesium methoxide is dissolved in methanol or in a mixture of methanol and trichlorotrifluoroethane (FREON<sup>TM</sup> TF). Carbon dioxide is then introduced into the solution to produce a colourless 20% methoxymagnesium methylcarbonate solution. The resultant solution is very tolerant of water compared to solutions of magnesium methoxide and does not cause plugging of spray nozzles or gumming of brushes.

Canadian Patent Number 1,147,510 (Smith, R.D., June 7, 1983) describes another method for production of methoxymagnesium methylcarbonate. Magnesium metal is reacted with absolute methanol to produce dried magnesium methoxide. The magnesium methoxide is then re-dissolved in methanol containing carbon dioxide to produce a solution of methoxymagnesium methylcarbonate. The solution is diluted with trichlorotrifluoroethane or dichlorodifluoromethane. The diluted solution is sprayed or brushed onto papers to

deacidify the paper. Alternatively, the paper can be dipped into the solution. This method for preparation of methoxymagnesium methylcarbonate allows the dry material, namely magnesium methoxide, to be prepared prior to  
5 delivery to a work site and then re-dissolved in methanol and reacted with carbon dioxide on site.

United States Patent Number 4,860,685 (Smith, R.D., August 29, 1989) and corresponding Canadian Patent Number 1,272,018 (July 31, 1990) describe a soft spray system for  
10 deacidification of cellulosic materials. A deacidification agent, preferably a carbonated magnesium alkoxide, is combined with a chlorofluorocarbon diluent, preferably trichlorotrifluoroethane, and a chlorofluorocarbon gas propellant, preferably dichlorodifluoromethane. Additional  
15 pressurizing and propelling may be provided by an inert gas such as nitrogen. The carbonated magnesium alkoxide, such as methoxymagnesium methylcarbonate or ethoxymagnesium ethylcarbonate, is produced by dissolving the corresponding magnesium alkoxide in a lower alcohol in the presence of  
20 carbon dioxide.

The prior art processes described herein use chlorofluorocarbons since they are substantially unreactive and, as such, pose no direct toxic threat to living organisms. However, these very same characteristics that  
25 render chlorofluorocarbons inert pose significant problems in the stratosphere. Chlorofluorocarbons have been recognized as being a major factor responsible for stratospheric ozone depletion and for contributing to the greenhouse effect. Of particular concern is the chlorine  
30 which is liberated when the chlorofluorocarbons are exposed to strong UV radiation in the stratosphere. Chlorine depletes ozone by catalyzing its conversion to molecular oxygen. Production and consumption of chlorofluorocarbons has been substantially reduced and must be eliminated by  
35 January 1, 1996 (Copenhagen Agreement to amend Montreal Protocol, November 23-25, 1992). Accordingly, a substitute must be found for the chlorofluorocarbon diluent of the

prior art compositions.

It is an object of the present invention to provide a composition for deacidification of aging cellulosic material comprising a diluent to replace the  
5 chlorofluorocarbon diluents of the prior art.

#### SUMMARY OF THE INVENTION

According to one aspect of the present invention, there is provided a composition for deacidification of a  
10 cellulosic material, comprising a carbonated magnesium alkoxide, a solvent, and a hydrochlorofluorocarbon and/or a hydrofluorocarbon diluent.

According to another aspect of the present invention, there is provided a method for preparing a composition for  
15 deacidification of a cellulosic material, comprising the steps of refluxing magnesium metal in methanol to produce a suspension of magnesium methoxide in methanol; cooling the suspension of magnesium methoxide in methanol; saturating the cooled suspension of magnesium methoxide in  
20 methanol with carbon dioxide to produce a solution of methoxymagnesium methylcarbonate in methanol; and diluting the solution of methoxymagnesium methylcarbonate with a hydrochlorofluorocarbon or hydrofluorocarbon diluent.

#### 25 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, the chlorofluorocarbons of the prior art deacidification compositions are replaced with a hydrochlorofluorocarbon and/or a hydrofluorocarbon.

30 The present inventor has discovered that carbonated magnesium alkoxide deacidification agents are soluble in hydrochlorofluorocarbons and/or hydrofluorocarbons and that the resultant compositions are effective in deacidification of cellulosic materials. Moreover,  
35 hydrochlorofluorocarbons and hydrofluorocarbons are substantially inert and are not toxic.

The use of hydrochlorofluorocarbons and



hydrofluorocarbons to replace the chlorofluorocarbons of the prior art compositions substantially reduces the available number of chlorine ions which may be liberated upon exposure to strong UV radiation in the stratosphere, as compared with the prior art chlorofluorocarbons. Furthermore, the presence of hydrogen renders the compound more reactive so that it is more likely to be decomposed before it reaches the stratosphere. Moreover, the rate of decomposition is higher than that of chlorofluorocarbons which have a lifetime of about 60 to 100 years. While regulations will eventually prohibit the use of hydrochlorofluorocarbons, the phase-out schedule for consumption only begins on January 1, 1996 with elimination scheduled for 2030 (Copenhagen Agreement to amend Montreal Protocol, November 23-25, 1992). There are no such regulations in place with respect to hydrofluorocarbons.

The hydrochlorofluorocarbon and/or hydrofluorocarbon act as a diluent for delivery of a deacidification agent and a solvent to aging cellulosic materials. Hereinafter, the term "cellulosic material" will be understood to include paper, books, documents, archival records, maps, works of art and articles made from cotton and/or linen including clothing and flags.

A suitable deacidification agent is a carbonated magnesium alkoxide, such as methoxymagnesium methylcarbonate or ethoxymagnesium ethylcarbonate.

One method for production of methoxymagnesium methylcarbonate is described in United States Patent Number 3,939,091. Magnesium metal is refluxed in methanol to give a suspension of magnesium methoxide in methanol. After cooling, the suspension of magnesium methoxide in methanol is saturated with carbon dioxide to form a solution of methoxymagnesium methylcarbonate in methanol.

Methoxymagnesium methylcarbonate and ethoxymagnesium ethylcarbonate may also be produced as described in Canadian Patent Number 1,147,510 wherein magnesium metal is reacted with methanol or ethanol to produce magnesium

methoxide or magnesium ethoxide, respectively. The resultant solution is dried, by a method known to those skilled in the art, to form a dried powder of magnesium alkoxide. The dried magnesium methoxide or magnesium  
5 ethoxide is subsequently added to methanol or ethanol in the presence of carbon dioxide to form methoxymagnesium methylcarbonate or ethoxymagnesium ethylcarbonate, respectively.

Preferably, the carbonated magnesium alkoxide is  
10 methoxymagnesium methylcarbonate or ethoxymagnesium ethylcarbonate, with methoxymagnesium methylcarbonate being the most preferable. However, it will be appreciated by those skilled in the art that other suitable carbonated magnesium alkoxides can be prepared by either of the above-  
15 mentioned methods using other solvents to produce the corresponding homologs of methoxymagnesium methylcarbonate. The solvent must however be evaluated for the potential for damage to the bindings, inks, etc. of the material being treated.

20 The concentration of carbonated magnesium alkoxide in the solvent is suitably in the range of from about 5 to 20% (w/v). Preferably, the concentration is about 20% (w/v).

The resultant solution of carbonated magnesium alkoxide in solvent is diluted with a  
25 hydrochlorofluorocarbon and/or a hydrofluorocarbon to yield a concentration of carbonated magnesium alkoxide in the range of from about 0.1 to 2% (w/v). Preferably, the concentration of carbonated magnesium alkoxide in the diluted solution is in the range of from about 0.5 to 1.5%  
30 (w/v). The hydrochlorofluorocarbon and/or hydrofluorocarbon diluent contributes to rapid evaporation of the solution and minimizes attack on certain inks by the solvent. It is desirable that the concentration of solvent in the deacidification composition of the present invention  
35 is as low as possible. Preferably, the concentration of solvent in the diluted solution is less than about 5% (v/v).



Suitable hydrochlorofluorocarbon diluents are difluorochloroethane, trifluorochloroethane, tetrafluorochloroethane, hydrochlorofluoropropanes and hydrochlorofluorobutanes. A particularly suitable hydrochlorofluorocarbon diluent is 1,1-dichloro-1-fluoroethane. Chlorodifluoromethane may be added as a co-diluent to increase the vapour pressure of the mixture, thereby increasing evaporation of the solution. Preferably, the concentration of chlorodifluoromethane added as a co-diluent is not greater than about 10% (v/v), in view of the high vapour pressure of chlorodifluoromethane.

Suitable hydrofluorocarbons are fluorinated methanes, ethanes, propanes and butanes.

The deacidification composition of the present invention may also include additives, such as a plasticizer, to reduce the brittleness of the cellulosic material.

The deacidification composition of the present invention may be applied to cellulosic materials in a manner known to those skilled in the art, for example by spraying with a spray gun or an aerosol can, by brushing or by dipping the cellulosic materials into the deacidification composition.

Preferably, the method for deacidification of cellulosic materials is as follows.

The cellulosic materials are placed in a vessel capable of withstanding a vacuum. The vessel is sealed and evacuated with a vacuum pump. Preferably, the water content of the cellulosic materials is reduced from a normal equilibrium moisture content of from about 5 to 6% to a residual moisture content of from about 1 to 2% under vacuum. The deacidification composition of the present invention is then introduced to the vessel and the cellulosic materials are immersed in the composition for a time sufficient to allow penetration of the composition into the cellulosic materials.

If desired, a positive pressure, for example by introduction of carbon dioxide or another gas, may be applied to the vessel to increase the penetration of the composition.

5       The treatment may be conducted at room temperature or greater. It will be appreciated by those skilled in the art that the temperature must not be so great as to damage the cellulosic material being treated.

10       At the end of the treatment, the vessel is drained and a vacuum is applied to the vessel to recover any remaining solvent and diluent. The cellulosic material is then removed from the vessel and is allowed to air dry in a fumehood. This method is particularly advantageous in that it permits simultaneous treatment of a large number of  
15 books, for example. Furthermore, the solution can be readily recovered from the vessel.

      Alternatively, the deacidification composition of the present invention may be applied by the soft spray system described in United States Patent Number 4,860,685,  
20 discussed hereinabove. It will be appreciated by those skilled in the art that other methods of contacting the cellulosic materials with the deacidification composition of the present invention are also suitable. For example, it is not necessary that the cellulosic material be dried  
25 under a vacuum prior to contacting with the deacidification composition of the present invention. The cellulosic material may also be contacted with the deacidification composition of the present invention by brushing or spraying.

30       The deacidification composition of the present invention may also be used in the method and apparatus described in Canadian Patent Application Number 2,009,621 (Eggersdorfer, R. et al, published August 11, 1990). Canadian Patent Application Number 2,009,621 relates to a  
35 method and apparatus for deacidification of cellulosic materials by pre-drying the paper by high frequency radiation in a vacuum, neutralizing with a deacidification

2142195

solution and evaporating the solvent in a vacuum with high frequency radiation. The apparatus described is a single treatment chamber for the pre-drying, neutralizing and evaporating steps in an enclosure for total solvent  
5 recovery.

## CLAIMS:

1. A composition for deacidification of a cellulosic material, comprising a carbonated magnesium alkoxide, a solvent, and a hydrochlorofluorocarbon and/or a hydrofluorocarbon diluent.
2. A composition according to claim 1, wherein the hydrochlorofluorocarbon diluent is selected from the group consisting of difluorochloroethane, trifluorochloroethane, tetrafluorochloroethane, hydrochlorofluoropropanes and hydrochlorofluorobutanes.
3. A composition according to claim 2, further comprising chlorodifluoromethane as a co-diluent.
4. A composition according to claim 3, wherein the concentration of chlorodifluoromethane is not greater than about 10% (v/v).
5. A composition according to claim 1, wherein the hydrofluorocarbon diluent is selected from the group consisting of fluorinated methanes, ethanes, propanes and butanes.
6. A composition according to claim 1, wherein the carbonated magnesium alkoxide is methoxymagnesium methylcarbonate.
7. A composition according to claim 1, wherein the carbonated magnesium alkoxide is ethoxymagnesium ethylcarbonate.
8. A composition according to claim 1, wherein the concentration of the carbonated magnesium alkoxide is in the range of from about 0.1 to 2% (w/v).
9. A composition according to claim 1, wherein the concentration of the carbonated magnesium alkoxide is in

the range of from about 0.5 to 1.5% (w/v).

10. A composition according to claim 1, wherein the solvent is methanol.

11. A composition according to claim 1, wherein the solvent is ethanol.

12. A composition according to claim 1, wherein the concentration of solvent is less than about 5% (v/v).

13. A method for preparing a composition for deacidification of a cellulosic material, comprising the steps of refluxing magnesium metal in methanol to produce a suspension of magnesium methoxide in methanol; cooling the suspension of magnesium methoxide in methanol; saturating the cooled suspension of magnesium methoxide in methanol with carbon dioxide to produce a solution of methoxymagnesium methylcarbonate in methanol; and diluting the solution of methoxymagnesium methylcarbonate with a hydrochlorofluorocarbon or hydrofluorocarbon diluent.

14. A method according to claim 13, wherein the hydrochlorofluorocarbon diluent is selected from the group consisting of difluorochloroethane, trifluorochloroethane, tetrafluorochloroethane, hydrochlorofluoropropanes and hydrochlorofluorobutanes.

15. A method according to claim 14, wherein chlorodifluoromethane is used as a co-diluent.

16. A method according to claim 15, wherein the concentration of chlorodifluoromethane is not greater than about 10% (v/v).

17. A method according to claim 13, wherein the hydrofluorocarbon diluent is selected from the group consisting of fluorinated methanes, ethanes, propanes and butanes.

2142195

18. A method according to claim 13, wherein the concentration of methoxymagnesium methylcarbonate in the diluted composition is in the range of from about 0.1 to 2% (w/v).

19. A method according to claim 13, wherein the concentration of methoxymagnesium methylcarbonate in the diluted composition is in the range of from about 0.5 to 1.5% (w/v).

20. A method according to claim 13, wherein the concentration of methanol in the diluted composition is less than about 5% (v/v).



**This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record.**

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☒ **BLACK BORDERS**

☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☐ **FADED TEXT OR DRAWING**

☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☐ **SKEWED/SLANTED IMAGES**

☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☐ **GRAY SCALE DOCUMENTS**

☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**

☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**